

## Operation of the Bruker M4 Tornado X-Ray Fluorescence Spectrometer

### 1 Introduction

The Bruker M4 Tornado is an energy dispersive x-ray fluorescence (EDXRF) spectrometer with fine focus and microspot analytical capabilities. These techniques are used for the analysis of specimens that are too small for bulk x-ray fluorescence analysis methods.

### 2 Scope

This document applies to personnel using the associated instrument(s)/equipment in support of metallurgy, anthropology, polymeric, or general chemistry examinations. The operation of the Bruker M4 Tornado will follow the procedures outlined in the current revision of Chemistry Unit (CU) Metallurgy standard operating procedure (SOP) *Compositional Analysis by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF)* and the specific parameters described below.

### 3 Principle

The Bruker M4 Tornado has two excitation options to generate the incident x-ray beam:

- 1) a rhodium target, microfocus x-ray tube (50 kV, 30W max) with a polycapillary lens delivering a 25  $\mu\text{m}$  spot (microspot EDXRF), or
- 2) a molybdenum target, fine focus x-ray tube (50 kV, 40W max) with a 1.0 mm fixed collimator (collimated EDXRF).

A silicon drift detector (SDD) measures photons emitted by the specimen. These components are arranged in a top-down configuration, with a working distance of approximately 10 mm.

Specimens are placed face up on an adjustable stage for measurement. Elements with atomic number equal to and greater than 11 (sodium) can be measured. Measurements can be made in air or under vacuum.

Video cameras provide specimen surface images at approximately 10X and 100X magnification and a chamber image to aid in positioning the specimen for measurement. Instrument control and data analysis are performed using ESPRIT software running on a personal computer that is connected to the analyzer.

## 4 Specimens

Specimens as small as 25  $\mu\text{m}$  in diameter can be examined using the instrument. Smaller specimens may produce sufficient x-ray emission for measurement if they are positioned within the circle on the video screen aligned with the x-ray optic. If quantitative results are desired, it is necessary to prepare the specimens so that they have a flat, smooth surface. The specimens must also be sufficiently thick to allow reliable quantitation. Liquid specimens can be contained in a plastic cup. The flat, upper surface of the liquid will provide the required analysis surface.

## 5 Equipment/Materials/Reagents

- a. Bruker M4 Tornado microspot EDXRF
- b. Performance check standards:
  - i. Bruker “Nano” standardization block or any commercially pure manganese reference material
  - ii. FBI-B002 reference block or other zirconium reference material
- c. Mounting materials (optional):
  - i. Graphite planchet
  - ii. Durotak sample mounting adhesive
  - iii. Plastic specimen cups (for liquids)
  - iv. Chemplex X-Ray Mylar (2.5 $\mu\text{m}$  thick) or polypropylene film (6.3  $\mu\text{m}$  thick) or similar
- d. Reference materials of alloys similar to the type(s) under analysis for alloy grade identification
- e. Certified reference materials (CRMs) of alloys similar to the type(s) under analysis for elemental quantitation or establishing limit of detection (LOD)

## 6 Standards and Controls

Manganese and zirconium standards are used to adjust energy output and to verify adequate performance of the instrument. Reference materials are often used to demonstrate the discernment of major, minor, and trace elements in alloys similar to the specimen under the same measurement conditions. Quantitative analyses will be appropriately validated using CRMs.

## 7 Sampling

Specific regions or objects may be chosen for compositional analysis. Refer to the specific case work SOP(s) for appropriate sampling procedures.

Small, heterogeneous particulate matter, like soil or fines, is not typically analyzed in bulk in the Bruker M4 Tornado. Rather, individual particles may be selected for analysis.

## 8 Procedure

### 8.1 Basic Operation

The basic operation from a powered-down condition consists of the following steps.

- a. From a cold start, turn on the power to the computer and instrument.
- b. Open the control software (“M4” icon) and follow the on-screen prompts. Several modes that define regions of acquisition are available including Point, Line and Area modes (tabs at top of screen).
- c. If the instrument power has been off longer than 2 weeks, condition each tube to be used at 15 kV, 300  $\mu$ A for 5 minutes followed by 25 kV, 300  $\mu$ A for 5 minutes before operating at higher power.
- d. Position a specimen using the software drag bars or by entering known position locations. **WARNING:** The stage motion controller adjusts z height first. Assure that specimens will clear the tube guard by moving in x and y directions at low z, then adjust the z-height separately. Should the proximity sensor on the tube guard be activated, reset the motion controller by selecting “Reference all” on the “Stage” tab. Specimen height must be incorporated in determining stage height to achieve desired working distance.
- e. Verify energy scale linearity:
  - i. Use either tube with no filter, in air or vacuum.
  - ii. In Point mode, acquire signal for 100 s live time on a Zr standard (FBI-002 block or other Zr reference material.)
  - iii. Identify the position of the maximum height of the Zr  $K\alpha$  peak. If this energy differs by more than  $\pm 0.05$  keV from the expected peak energy of 15.746 keV (the weighted average of the Zr  $K\alpha 1$  and Zr  $K\alpha 2$  emissions), then perform an energy adjustment.
  - iv. Energy adjustment: Open the System tab, then Spectrometer tab. Highlight Zr  $K\alpha$ , select pulse rate of 130,000 cps, and energy ranges of 20 kV and 40 kV. Select Medium (precision), then “START”.

- v. Verify the position of the Zr K $\alpha$  peak maximum as above. If repeated failure of the energy adjustment routine occurs, the instrument may have to be serviced to correct the problem.
  - vi. Record the verified Zr K $\alpha$  peak position in the instrument log.
- f. Verify energy resolution:
- i. Use either tube at full power with no filter, in air or vacuum.
  - ii. Position a Mn standard (Bruker “Nano” standardization block or other Mn CRM) for measurement.
  - iii. Open the System tab, then Spectrometer tab. Select Mn K $\alpha$ , 130,000 cps pulse rate, 40 kV, Medium (precision), then “TEST”.
  - iv. Run long enough to allow the FWHM (full width-half maximum) value to stabilize to one decimal place. If the FWHM value exceeds 148eV, instrument service may be required.
  - v. Record the Mn K $\alpha$  FWHM value in the instrument log.
- g. Verification of the energy linearity and resolution are performed each day prior to the instrument being used for casework. Instrument performance can be re-verified during a long course of testing at the operator’s discretion. Energy adjustment of the instrument will be undertaken whenever the x-ray peak positions differ by more than  $\pm 0.05$  keV from their theoretical positions.

## 8.2 General Analysis

- a. Insert the specimen(s). In Point mode, align the area of interest at the center of the circle displayed on the video image at 10X magnification. Rough surfaces must be placed so that a working distance of ~10 mm can be achieved at the region to be analyzed without obstruction from neighboring high points. For a liquid specimen, the surface of the liquid should be within 2 mm of the top of the specimen cup.
- b. Select the appropriate measurement atmospheric condition: air or vacuum. Liquids or vacuum sensitive materials must be tested in an air atmosphere. To test in vacuum, select the vacuum icon.
- c. Focus the area to be measured at 100X magnification. An autofocus function is available through an icon adjacent to the video output.
- d. Select the appropriate x-ray tube, tube voltage and current to achieve a dead time of approximately 30% when collecting a spectrum. Acquisition parameters and filters can be adjusted to optimize the analysis conditions. An aluminum alloy, carbon steel and a silver alloy, for example, would all require different operating conditions for optimal results. A set of useful, basic analysis conditions can be found in the Instrumental Conditions

section. It is typical to analyze materials of atomic number 22 (Ti) and below under vacuum atmosphere.

- e. Acquire a spectrum for an appropriate duration to collect sufficient counts for analysis. Acquisition times will depend on the conditions chosen, the material analyzed and the specimen area exposed to the incident beam.
- f. Identify the peaks present in the spectrum using the interactive periodic table in the analysis software. Software-generated identifications must be interpreted by an experienced operator to prevent misidentification of energy peaks. The system software automatically filters the escape peaks of predominant elements from the spectral display. Refer to *Compositional Analysis by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF)* for more details regarding peak labeling.
- g. Print an individual spectrum using the innermost IMPORT-EXPORT menu, print command. This command will generate the filename and acquisition conditions on the printout. Write the resulting percent dead time on this printout. (Although dead time is saved within the raw data file, it will not print automatically.) To print multiple overlaid spectra, highlight and checkmark all of the spectra from the viewing window list before selecting the print command from the innermost IMPORT-EXPORT menu. If not printed on separate, individually printed spectra, record the acquisition conditions for the multiple, overlaid spectra in the case notes.
- h. Ensure the tube power returns to standby (20kv, 50μA) after testing is completed. If the instrument will be unused for two or more days, shut off the x-ray tube. Close the software.

### 8.3 Quantitation of Data

The spectra acquired from a specimen can be processed to yield weight concentrations of the elements detected. If numerical compositional data is to be reported, validation must be performed on the same instrument under the same operating conditions using CRMs with a matrix similar to that of the specimen of interest. The ESPRIT analysis software contains several methods for quantitative analysis, including standardless fundamental parameters-based and standards-based analysis.

## 9 Instrumental Conditions

Table 1 contains a set of basic analysis conditions that have been found to be useful for preliminary screening of materials. Other conditions are permissible and will be determined by the operator based on analytical objectives.

Table 1: Basic Operating Parameters for Analysis

<u>Control Tab</u>	<u>Parameter</u>	<u>Value</u>
Spectrometer	Maximum energy	40keV
	Mode	Normal operation
	Cooling	Thermostat
X-ray tube 1 (microfocus tube)	Voltage	40 kV
	Current	250 $\mu$ A
	Filter	none
Acquire	Range	40 keV (provides ~10 ev/channel)
	Preset	100 seconds
(Top left icon)	Atmosphere	Vacuum

## 10 Decision Criteria

### 10.1 Instrument Performance

During analysis, energy adjustment of the instrument will be undertaken whenever the x-ray peak positions differ by more than  $\pm 0.05$  keV from their known positions.

### 10.2 Spectral Analysis

General decision criteria for peak identification, spectral comparison and quantitative EDXRF analysis are described in *Compositional Analysis by X-ray Fluorescence Spectrometry (EDXRF)*. Additional considerations particular to this instrument are:

- The Bruker M4 Tornado microfocus x-ray tube with polycapillary lens generates a Bremsstrahlung excitation spectrum that tails off at the higher end of the spectrum. This inhibits fluorescence of lines with absorption energies greater than 30keV, regardless of any further increase in tube voltage. This can result in significantly higher limits of detection for K line emissions from elements with atomic number of approximately 48 and higher. Conditions may be adjusted to optimize the L and M lines emissions from these elements to aid detection.
- Each tube will produce its own characteristic energy peaks, e.g., the rhodium x-ray tube should not be used if Rh is expected to be in the specimen and conversely, Rh should not be reported to be present in the specimen unless verified. The Mo x-ray tube can be used for verification.
- The geometry of the tube-specimen-detector arrangement creates diffraction peaks from crystalline materials (including metals). These artifacts in the compositional spectra can usually be readily differentiated from x-ray fluorescence peaks because diffraction peaks appear broader across the energy axis and because their positions often differ from

known atomic emissions. When using the microfocus polycapillary tube to analyze steels, the Bruker M4 Tornado often presents a small diffraction peak near 3.5 keV.

## 11 Calculations

See *Compositional Analysis by X-ray Fluorescence Spectrometry (EDXRF)* for applicable calculations.

## 12 Measurement Uncertainty

Typically, the Bruker M4 Tornado is not used for quantitative analysis. In the event that it is necessary to estimate the measurement uncertainty of an instrumental result, it will be done in accord with the *Chemistry Unit Procedures for Estimating Measurement Uncertainty*.

## 13 Limitations

*Compositional Analysis by X-ray Fluorescence Spectrometry (EDXRF)* contains general limitations of compositional measurement by x-ray fluorescence spectrometry. Additional limitations specific to this instrument are:

- a. Vacuum sensitive samples, like liquids, that are suspected of containing elements with atomic number  $Z < 22$  (Ti) cannot be measured in the Bruker M4 Tornado. These can be measured in a system offering a helium overpressure atmosphere.
- b. Spectral artifacts, including diffraction peaks, must be considered during analysis. (See Spectral Analysis section).

## 14 Safety

- a. The Bruker M4 Tornado produces x-rays. Wear an x-ray film badge or dosimeter when operating this instrument. The instrument has a protective enclosure with internal safety interlocks to prevent inadvertent x-ray radiation exposure. Never bypass or disable the safety interlocks on this instrument.
- b. The detector and tube windows are comprised of beryllium and are extremely delicate. In the event of damage to a window, the beryllium dust created could pose an acute health hazard. If this occurs, seal the chamber and seek assistance from the Laboratory Health and Safety Group.

## 15 References

Jenkins, R., *X-ray Fluorescence Spectroscopy*, Wiley Interscience, New York 1988

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Margui, E. and Van Grieken, R., *X-Ray Fluorescence Spectrometry and Related Techniques*, Momentum Press LLC, New York 2013

*Chemistry Unit Quality Assurance and Operations Manual*, Federal Bureau of Investigation, Laboratory Division, latest revision

*Compositional Analysis by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF)*, Metallurgy Manual 500, Chemistry Unit, latest revision



Rev. #	Issue Date	History
2	03/02/2018	Renumbered Metallurgy SOP Manual documents. This document was formerly Metal 27 and is now designated Metal 502. Added personnel to section 2. Clarified application of instrumental conditions, Section 9. Made minor editorial corrections throughout document. Added requirement for sampling plan retention in section 7. Revised sections 8.1.e and 8.1.f to clarify instrument verification procedure. Added instrument shut-down directions in section 8.2.h. Added section 10.2.b to clarify x-ray tube influence. Updated safety requirements in section 14. Added additional references to section 15.
3	08/16/2021	Edited Scope to include polymeric exams. Changed “sample” to “specimen” or “material” as appropriate. Referred to casework SOPs for Sampling. Clarified Decision Criteria. Added reference to <i>Compositional Analysis by X-ray Fluorescence Spectrometry (EDXRF)</i> in Calculations section. Clarified application to small particulate material. Differentiated the application of CRMs v. reference materials in the Equipment section. Removed overt references to FBI Laboratory over-arching quality documents.

### **Approval**

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